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(54) PRODUCTION AND RECOVERY OF CHEMICAL VALUES FROM WASTE SOLIDS

(71) We, OCCIDENTAL PETROLEUM CORPORATION, a Corporation organised and existing under the laws of the State of California, United States of America, of 10889 Wilshire Boulevard, Los Angeles, California, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention concerns the production and recovery of chemical values from waste solids.

The disposal of both industrial and domestic waste solids (colloquially called trash, rubbish, garbage, etc. and collectively called "trash" herein) is becoming an immense problem. The cost of this service presently ranks third behind public schooling and highways as a municipal expense in the United States. The cost per unit of trash disposal and the number of units of trash per person are rising annually. It is estimated that each individual in the U.S.A. generates 4—6 pounds per day of solid waste, and that the industrial output is equivalent to approximately five pounds of solid waste per person per day. The cost of disposal varies from 5 to 30 dollars per ton of trash. Previous methods of trash disposal, such as land fill are becoming impossible, while others such as incineration are costly and result in air pollution problems. Less costly and more efficient disposal means for solid waste appear mandatory.

A second aspect of this problem is that the world is consuming its natural resources at an ever increasing rate. In the normal materials utilization cycle, raw materials are collected, processed into useful products, utilized by consumers for varying spans of time, and then consigned to a presumably uncovered wasteland, the city dump.

Because of these problems, many proposals have been put forth to utilize and recover values from solid wastes. Aluminium companies and glass companies will purchase used

cans and bottles for reprocessing. Engineering studies and plant designs have been prepared to advance the concept of utilizing the heat produced by garbage incineration to operate electrical and desalination plants.

The recovery of metal values from waste solids is old in the art and is an integral part of the steel-making industry.

However, the art must now develop processes to utilize both the metallic and non-metallic portion of waste solids as a raw material since these represent a large portion of the waste solids. Simple incineration of the organic portion of waste solids to produce utilizable heat is not the solution for several reasons. The off gases produced during incineration contain air pollutants, such as SO₂, NO_x, CO and ash. These pollutants must be trapped or diminished which requires costly devices such as electrostatic precipitators, scrubbers, etc. to avoid air pollution. In addition, organic waste solids are a poor fuel, and require very high combustion temperatures. What is needed is an efficient, economical method for handling the conventional waste solids produced by society which will recover chemical and fuel values from both the inorganic and organic portions of waste solids while substantially reducing the volume of gaseous effluent which must be treated to eliminate air pollution during processing.

At the present time, a significant amount of discarded raw materials is being recycled to the economy by many companies engaged in America's secondary materials industry. Large quantities of metals, an appreciable amount of paper, and some glass is being collected, upgraded and reused. However, except for tin and aluminium cans in some scattered areas of the nation, only a small fraction of the reuseable resources of the U.S.A. are being recovered once they enter the municipal collection stream. A typical breakdown of municipal refuse is shown in the following Table 1, and up to now the difficult problem has been how to separate the vast amount of

contaminated materials from the heterogeneous mass, and recover the potential values shown in this Table.

TABLE 1
Recoverable Materials in Municipal Solid Wastes

Raw Material	Composition Wt. %	Estimated Recovery Eff. %
Group 1		
Magnetic metals	6—8	95
Non-magnetic metals	1—2	95
Glass	6—10	80
Dirt and debris	2—4	—0—
Subtotal		
Group 2		
Paper products	48—55	50
Group 3		
Unreclaimed paper and other organics	~55	100

We have invented a process aimed at overcoming the above problems.

Thus the invention provides a process for the production and recovery of chemical and fuel values from waste materials containing organic solids, comprising forming a turbulent stream (as herein defined) by entraining hot particulate char and particulate waste material in an inert carrier gas (as herein defined); passing said stream through a pyrolysis zone at a rate such that the entrained solids remain in said zone for an average residence period not exceeding 10 seconds during which heat exchange takes place between the char and the waste material particles and the latter are heated to a pyrolysis temperature in the range 150 to 1400°C. to evolve volatile organic chemical and fuel values; and removing said chemical and fuel values from the stream leaving said pyrolysis zone. Preferably said removed organic chemical and fuel values are rapidly cooled to a temperature below the pyrolysis temperature so that degradation of said organic chemical and fuel values by further pyrolysis is minimized.

By appropriate management, the process can convert the unusable organic portion of a wide range of waste materials to clean-burning, low-sulphur heating fuel. For instance, over one barrel of good quality, liquid heating fuel can be obtained per ton of wet as-received municipal refuse.

The process is based upon the rapid heating of particulate, e.g. shredded, organic waste materials in the absence of air using solid to solid heat-exchange between particles entrained in a flowing carrier gas stream. Bench-scale and pilot plant trials have resulted in liquid organic chemical and fuel (oil) yields of greater than 40 weight percent

being obtained from oven-dried, inorganic-free feed material, this oil having an average heating value of about 12,000 Btu per pound and being usable as a low-sulphur replacement for No. 6 fuel oil.

Pyrolysis of organic waste materials by the process of the invention also produces char, gases, and a water fraction. The distribution of these products is the most important economic factor involved in any commercial pyrolysis process. Most other prior art processes produce relatively little organic liquids unless high pressure hydrogenation is employed. An example of the distribution and analysis of the products which can be obtained by means of the process of the invention is shown in the following Table 2.

TABLE 2
Products of Pyrolysis

Char fraction, 20 wt. %	Heating value 9,000 Btu/lb	
48.8 wt. %	Carbon	
3.9	Hydrogen	
1.1	Nitrogen	
0.3	Sulphur	85
31.8	Ash	
0.2	Chlorine	
13.9	Oxygen	
	(by difference)	
Oil fraction, 40 wt. %	Heating value 10,500 Btu/lb	
57.5 wt. %	Carbon	
7.6	Hydrogen	
0.9	Nitrogen	
0.1	Sulphur	95
0.3	Ash	
0.3	Chlorine	
33.3	Oxygen	
	(by difference)	
Gas fraction, 27 wt. %	Heating value 550 Btu/cu.ft.	
0.1 mol %	Water	
42.0	Carbon monoxide	
27.0	Carbon dioxide	
10.5	Hydrogen	105
<0.1	Methyl chloride	
5.9	Methane	
4.5	Ethane	
8.9	C ₃ to C ₇ hydrocarbons	

Water fraction, 13 wt. %	
Contains:	
Acetaldehyde	Methanol
Acetone	Methylfurfural
Formic Acid	Phenol
Furfural	Etc.

Aside from the organic liquid (oil) yield of 40 wt. % obtained in a typical run, about 20% char, 27% gases and 13% water are

also obtained, as indicated by the above Table. However, the gases and some of the char are conveniently utilized as carrier gas and as a heat source in carrying out the process, while the residual char, like the organic liquid, is salable for use as a fuel or raw chemical.

The pyrolysis process is flexible with regard to feed materials. So far, the following waste products have been converted to useful chemical and fuel liquids and chars: tree bark, rice hulls, animal feed lot wastes, and shredded automobile tires. In the case of tires, the char produced is recyclable into new tire manufacture as a carbon black substitute. Tests show that modules of elasticity and tensile strength of rubber compounded with this char, approach to within 75 to 85% of the values of these properties obtained when rubber is compounded conventionally with general purpose carbon black.

In preferred practice of the process of the invention, the waste material fed to the pyrolysis zone in the gaseous stream has a particle size not greater than about 1.0 inch.

In the process organic chemical solid-values in the waste material are volatilized and pyrolyzed by heat to organic chemical values which are eluted from the inorganic solids in the vapour phase and rapidly removed therefrom to minimize thermal decomposition of these values. The organic chemical and fuel values emerging from the pyrolysis zone may be readily separated from the inorganic portion of the pyrolyzed waste material solids by conventional classification systems. The process may be beneficially utilized to recover chemical values from waste solids which are essentially organic in nature. The organic chemical effluent from the pyrolysis zone contains a raw material suitable for further processing as will be indicated hereinafter. That is to say, the volatile organic values, which are a valuable raw material, can be separated from the other products of the pyrolysis zone and from the carrier gas and be further treated to produce useful products. Metallic values in the segregated inorganic solids can be recovered therefrom by conventional processing.

The process of the invention is intended for dealing with the conventional solid wastes, containing organic matter, produced in our society. Municipal solid wastes can contain the widest variety of ingredients, e.g. glass, metal, water, organic products such as paper, automobile tires, plastics and vegetable and animal material. Industrial wastes include rubber, plastics, agricultural wastes, manure, waste wood products and cannery wastes. The invention provides a process for the conversion and/or volatilization of the organic material in such solid wastes to useful organic chemical and fuel values, such as hydrocarbons and oxygenated hydrocarbons. While

the process can handle conventional waste solids without prior separation of the inorganic matter therefrom, preferably the bulk of the inorganic materials are first separated from the waste solids and only that portion of the waste solids which is composed substantially of organic (carbonaceous) materials or matter is treated by the process. The degree of segregation of organic matter from the original waste solids is variable, since total segregation may impose uneconomical cost factors on the overall process.

Waste solids can be segregated by using conventional separation equipment and processes. The presence of water in the organic wastes is preferably kept to a low value (from about 0 to about 5%), since its presence creates an aqueous fraction in the volatiles recovered in the process and imposes an extra heat load. The aqueous fraction will contain organic solvents such as alcohols, ketones, aldehydes and acids which create an additional separation problem for recovery. Large quantities of water can be easily removed from the waste solids by conventional means, such as heating in a predrying process.

The waste material solids, segregated or unsegregated, are comminuted to a particulate form, the maximum dimension of the particles preferably being no greater than one inch, and in the preferred embodiments the particles of the comminuted waste solids have a maximum dimension of 0.25 inch or less. By the term "maximum dimension" is meant the largest dimension, e.g. either length or width or thickness, of the individual particles which should not exceed this upper limit. The individual particles may have smaller dimensions and may consist of chunks having essentially three dimensions, or may consist of pieces of paper, plastic film, plant leaves having essentially two dimensions and/or they may comprise strips of material e.g., organic filaments which have essentially one dimension. The size and shape of the particles as well as the density will affect the pressure drop within the system and the heat transfer into the particles which will necessitate adjustments of residence times within the pyrolysis zone to ensure that the particles of organic matter are heated to the desired reaction temperature in the zone. For these reasons and to avoid the need for repeated adjustment of process conditions it is preferable that the waste solids be comminuted and intermixed to produce a substantially uniform mixture.

An essential feature of the process of this invention is the rapid heating of the organic waste material solids to a temperature in the range 150—1400°C., preferably from about 315 to about 565°C. (an especially preferred range being from about 425 to about 510°C), while the waste solids are entrained in a turbulent gaseous stream composed of carrier

gas, waste material solids and hot particulate char. The selection of a particular temperature will however be dependent upon the particular organic waste material solids employed and the residence time of the waste solids in the pyrolysis zone. The heating of the waste material solids takes place while the stream is contained within a pyrolysis zone for a period which is generally substantially less than 10 seconds and is preferably from about 0.1 to about 0.6 seconds. In general we have found that organic waste material solids from municipal sources can be advantageously treated by the process of the invention by heating the organic waste material solids to a temperature ranging from between about 425 to about 540°C. in the pyrolysis zone with a residence time ranging between 0.1 to 2 seconds. When the process is so conducted that the organic solids are heated to a temperature of about 485°C. in the pyrolysis zone a residence time of from about 0.3 sec. to about 1.3 sec. is preferred. When wastes containing at least 70% cellulosic material is used, a temperature of from about 425 to about 455°C. is preferably used with a residence time of about one second or less. When wastes composed of automobile tire particles are processed, lower temperatures e.g., about 150 to about 260°C. may be employed. The relationship between temperature and residence time can be varied to optimize yields of the liquid organic chemical and fuel values. If the temperature and/or residence times are too low, the vaporization and pyrolysis of the waste material organic solids is incomplete. When the temperature and/or residence time is too high, the pyrolysis products are degraded, giving low yields of liquid chemical and fuel values.

By the term "turbulent stream" is meant a stream of gas that, when flowing through the pyrolysis zone, e.g. a pipe shaped reactor vessel, has a flow that is turbulent in nature, e.g. having a Reynolds flow Index Number greater than 2000 and preferably about 2500.

In operation, a low ratio of about 0.2 to about 2.0 pounds of mixed gases to each pound of waste solids is all that is required to obtain a Reynolds flow Index Number of 2000 or greater when the flow passage defining the pyrolysis zone has a diameter or equivalent dimension of 3 inches or greater. For example, with a 10 inch diameter pyrolysis zone flow passage, about 0.7 pounds of gas for each pound of solids is all that is required to maintain a turbulent flow in the zone. Laminar flow in the pyrolysis zone must be avoided because such a flow system tends severely to limit the productivity and rate of heat transfer within the pyrolysis zone. In the normal practice of this invention the carrier gas, hot char and waste material solids are introduced into one end of a pyrolysis vessel and rapidly intermixed and dynamically

contacted with each other as they are blown through the vessel to permit the requisite heat transfer to take place.

The heat required to pyrolyze the organic matter and remove the volatile organic chemical values can be provided wholly or only in part by the sensible heat in the hot char particles, but preferably substantially all the heat is supplied by hot char. From about 2 pounds to about 10 pounds of hot char is preferably used for each pound of solid waste. The use of hot char as the heat source in the pyrolysis zone has many advantages. Because of its heat capacity and density, a much lower volume of char is needed to heat the solid waste than would be the case if hot carrier gas alone was used. The hot char comes into intimate contact with the solid waste in the turbulent gaseous stream for efficient solid to solid heat transfer.

The selection of an optimum char-to-waste solids weight ratio will of course be dependent upon the heat transfer requisites of the system. Since part of the heat of pyrolysis can be supplied by the carrier gas, the temperature, flow rate and residence time in the reactor may be calculated by well known methods for a particular system.

Heat energy can also be furnished to the pyrolysis zone by indirect means such as electrical heating through the zone wall.

The carrier gases found usable in the process of this invention to effectuate the thermal elution of the waste solids particles are those which are non-reactive with the char, with the organic matter and with the organic chemical values formed during pyrolysis. The carrier gas stream should be substantially free of air and oxygen, the stream preferably containing less than 4% oxygen, ideally less than 1% oxygen. The amount of oxygen is minimized to minimize oxidation of organic values including the liquid chemical and fuel values. Exemplary of gases suitable for use as carrier gases are, nitrogen, argon, CH₄, H₂, carbon monoxide, flue gases, carbon dioxide, but any other gas which will not deleteriously react with or oxidize the organic portion of the matter within the system may be used and the term "inert carrier gas" as used herein is to be understood as meaning a gas that meets these criteria. In preferred embodiments of the invention we recycle the carrier gas back to the pyrolysis zone after the organic chemical values, and certain other pyrolysis products, have been removed therefrom.

The effluent from the pyrolysis zone is composed of char, volatilized liquid organic fuel and chemical values, product gas, and carrier gas. In preferred practice, the volatilized liquid organic fuel and chemical values are forthwith cooled to a temperature below the temperature of pyrolysis to minimize degradation of the organic chemical

values. The char and any other solids can be readily separated from the gases and volatilized liquids by any conventional solids/gas separator such as a cyclone. The volatilized organic chemical values and carrier gas can be separated from one another and recovered by conventional separation and recovery means.

When the waste material solids passed through the pyrolysis zone contain inorganic matter such as metal and glass, particles thereof, intermixed with the char produced by the organic portion of the waste solids, appear in the effluent of the pyrolysis zone, but the organic and inorganic solids can be readily separated by conventional air classification systems. In fact the pyrolysis of the organic solids increases the density differential between such solids and the inorganic solids and actually facilitates their separation in the pyrolysis zone effluent. However, a mixture of effluent solids, containing both inorganic and organic (char) solids may be recycled through the pyrolysis zone to provide the necessary heat without prior separation. When the pyrolysis zone effluent solids are separated into inorganic and char fractions and char alone is recycled, the heat content of the inorganic solids may, if desired, be recovered in a manner to provide heat for the pyrolysis zone in order to increase the efficiency and economics of the system: for instance, the heat of the inorganic solids may be used to heat the recovered gases. However, hot inorganic solids recovered from the pyrolysis zone effluent are in an excellent form and condition for further processing by conventional processes to recover metallic or inorganic chemical values therefrom and this factor may make it more economic not to cool these solids, to provide heat for the pyrolysis zone, before submitting them to further processing.

The gases produced by pyrolysis of the waste solids in general contain condensable hydrocarbons, which may be recovered simply by condensation, and non-condensable gases such as carbon dioxide, carbon monoxide, hydrogen and methane and other hydrocarbon gases which are not recoverable by ordinary condensation means. The product gases also contain undesirable gaseous products such as NH_3 , HCl , H_2S and water which should be removed from the product gas stream by conventional means such as cooling and chemical scrubbing. After the condensable organic chemical values and the undesirable gaseous products have been removed from the product gases, the resulting gases can be utilized to provide process heat and be recycled as the carrier gas for the pyrolysis of further waste material.

Initially the process is started up by using hot char from other sources, but after waste material solids have been pyrolyzed in the

process, more than sufficient hot char is produced by that pyrolysis to enable the process to be self-contained and independent of an external source of hot char. Excess char can be readily utilizable in further processing to provide new materials, which enhances the total economics of the process, such as fuel for use in a power plant or a raw material source for the chemical industry. The excess char may, for instance, be briquetted by conventional means for utilization like coke.

Excess char produced by the process can also be degasified, if desired, by heating to temperatures ranging from about 650°C . to 980°C . or higher to evolve a hydrogen-rich gas which is saleable as premium fuel. The gas can be upgraded into pure hydrogen, or used for hydrotreating the heavier volatilized chemical values produced by the process.

Char degasification can be carried out by direct or indirect heating. In direct heating, the char is contacted with sufficient oxygen from a suitable source, such as air, to bring the stream by controlled combustion up to the desired degasification temperature. This can be accomplished in a transport reactor similar to the pyrolysis reactor or in a fluidized bed reactor.

Preferably, however the char is degasified by indirect heating to yield a gas stream containing 70 or more percent by volume hydrogen. This may be accomplished in a reactor similar to a tubular heat exchanger, in which the char is blown through the tubes in a dense or dilute phase and fuel is burned in adjacent tubes to supply the heat required for gasification. Alternatively, the same result can be accomplished by the combustion of fuel in tubes located in a fluidized bed of the char. After separating the residual solid, degassed, char from the evolved gases, the char is cooled for ultimate use as a high grade fuel.

When it is desired to produce a low sulphur char, from waste solids containing large amounts of sulphur, sulphur reduction can be accomplished during pyrolysis or subsequently, for instance by degasification of the resultant char.

Desulphurization during pyrolysis may be achieved by having a solid sulphur acceptor, such as lime or iron oxide, present in the zone during pyrolysis. The sulphur combines with iron oxide to form pyrrhotite which is magnetic and can be removed, in addition to any iron pyrite naturally present, from the product char by magnetic separation. This can conveniently be accomplished with minimum cooling of the char to conserve the heat requirements for recycling or further thermal processing of the char.

Desulphurization may also be achieved during pyrolysis by enriching the gas stream with hydrogen, preferably part of the

hydrogen released during a subsequent char degasification step. Hydrogen fed to pyrolysis zone reacts with sulphur to form hydrogen sulphide which may later be removed by conventional means such as scrubbing; hydrogen addition to the pyrolysis zone also enriches the volatilized hydrocarbons. In preferred embodiments of the invention we use a carrier gas containing at least 20% by volume hydrogen based upon the total volume of carrier gas used.

Desulphurisation may also be achieved by heating the resultant char to a suitably high temperature, e.g. 1350 to 1550°C., in a transport gas enriched with hydrogen. This treatment also effects degasification if the char has not been degasified prior to such treatment. The hydrogen in the gas reacts with the sulphur in the char to achieve sulphur reduction of the product char. As with desulphurization during pyrolysis, the hydrogen employed may be obtained by the recycle of off gases from char degasification, before or after purification.

The product char, direct from the pyrolysis zone or after degasification and already at an elevated temperature, may also merely be heated to about 1350 to 1550°C. at ambient pressures in a non-oxidizing environment for a period up to about 20 minutes to achieve a substantial sulphur content reduction in the char.

If, as is preferred, the char is degasified by indirect heating using a hydrogen-rich carrier gas, maintaining a pressure of from about 15 to about 100 psia during degasification promotes sulphur removal. Under these conditions char can be desulphurized as well as degassed within reaction times of about ten minutes. However, this desulphurization technique is most useful as a supplementary treatment when inorganic sulphur has been mainly removed during pyrolysis by a sulphur acceptor in the stream flowing through the pyrolysis zone.

The accompanying drawing illustrates schematically a typical embodiment of the present invention and is not intended to be a limitation thereof, the drawing showing the equipment for carrying out the process.

Referring to the drawing, shredded particulate waste material containing organic solids, or pulp from a dewatering press (not shown) enters a thermal elution unit through a line 2 having a feed hopper 4 for surge storage. This waste material feed is metered through a valve 6 and enters a line 8 where it is combined with a mixture of air from a blower 10 and recycled gas from a mixing vessel 12. The feed and mixed gases pass through a line 14 and are dried in a dryer 16 as required or economically desirable. The dried feed solids and gases then pass through a line 18 to a cyclone separator 20 to separate the dried feed solids from the gases. The gases

are removed through a line 74 and enter a gas purification unit 72. The dried feed solids leave the cyclone separator 20 through a line 22 and are stored in a surge vessel 24.

The dried waste solids are then metered into a pyrolysis system, indicated generally at 25, through a valve 26 and pass through a line 28 to a line 30 where they are combined with hot recycled gas from a line 99. The stream of hot gas and waste solids while being transported through the line 30 are combined with hot recycle char and volatile gases fed to the line 30 through a line 60. The stream of gases, char and feed solids then passes into a pyrolysis reactor vessel 32.

In the pyrolysis reactor vessel 32, the stream is highly turbulent preferably having a Reynolds Flow Index Number of about 2500 and containing 0.2 to 2.0 lbs. gas per lb. of the particulate waste solids and such an amount of char, typically at least 2 lbs. of char per lb. of waste solids, that the waste solids are heated, in this embodiment, to a temperature ranging from about 260°C. to about 815°C. by heat exchange with the hot recycle char, volatile gases and recycle gases. The organic matter in the waste solids is pyrolyzed and volatilized in the pyrolysis reactor vessel 32 to produce chemical and fuel values which are normally vaporized at the pyrolysis temperature to form product gases. The average residence of the entrained solids in the reactor vessel 32 is not more than 10 seconds and is usually substantially less, typically being less than one second.

A stream of gases and char is removed from the reactor vessel 32 through a line 34 to a cyclone separator 36 wherein the gases are separated from the char and removed through a line 76. The gases are cooled in a quench tower 78. The condensate from the quench tower 78 leaves through a line 80 and is pumped by a pump 82 into a line 84 which leads to an oil storage vessel (not shown). The non-condensed gases from the quench tower 78 exit through a line 86 and are further cooled in a condenser 88. The further cooled gases and condensed liquids leave the condenser 88 through a line 90 and pass into a phase separator 92. There are three phases present at this point; gas, oil, and water. The gas leaves the phase separator 92 through a line 93 and is compressed for recycling in a compressor 95. The compressed gases are returned to the pyrolysis system from the compressor 95 through a line 97, preferably after being heated. A portion of the compressed gases is fed directly into the pyrolysis reactor 32 through the line 99 and the line 30 as previously described. The remaining compressed gases are sent to the mixing vessel 12 and used to dry the waste material feed as described above. Additional fuel, or other waste heat may also be used for this drying step.

The water from the phase separator 92 is removed through line 94 and pumped by a pump 96 into a line 98 to be processed by conventional means in a waste water treatment facility 100. The water after treatment is then disposed of in a conventional manner. A portion of the separated water is also recycled to the quench tower 78 as a cooling medium. The oil from the phase separator 92 is removed through a line 102 and pumped by a pump 104 through a line 106 to the line 84 and thence to the oil storage vessel.

The char from the pyrolysis reactor vessel 32, separated from the entrained gases in the cyclone separator 36 as described, is removed by a line 38 to a char receiver 40. Some of the char is used to supply process heat, a portion of the char being directed by a distributing valve 42 from the char receiver 40 and via a metering valve 42a into a line 44. This process char is combined with combustion air from a blower 46 and a line 47, and fed into a char heater 48 via a line 49. A portion of the char is burned in the char heater 48 to raise the overall temperature of the char to about 870°C. The heated char is passed from the char heater 48 through a line 50 to a cyclone separator 52 where the combustion gases are separated from the hot char. The combustion gases are removed by a line 53 and combined with the hot compressed gas in the line 97 to be used for drying the waste material in the dryer vessel 16 as explained.

The hot char from the cyclone separator 52 is removed through a line 54 into a hot char storage receiver 56, from which it is metered into the pyrolysis system 25 by a valve 58 and the line 60 leading to the line 30.

The char from the char receiver 40 which is not used for process heat is directed by the valve 42 to a metering valve 42b and passed into line 48. This char is mixed with process water from a line 62, the water flashing into steam which entrains the hot char and carries it into a cyclone separator 64. The resulting steam (at a pressure of 150 psi) is removed from the cyclone separator 64 by line 70 and passed to the gas purification unit 72. The hot char from cyclone 64 enters a product char storage vessel 66 and is passed to a compactor or the like (not shown) through a valve 67 and a line 68.

As stated above, the waste material that can be handled by the process of the present invention includes municipal waste, industrial waste such as tree bark, scrap rubber, rubber grindings, old tire rubber, ground tire carcasses, sugar refinery waste, corn cobs, rice hulls, animal matter from slaughter houses or rendering plants, sawdust, crude oil processing waste, and the oily discharge obtained from the ships when they clean their tanks. Municipal wastes and waste from vegetable or plant raw materials contain more than

70% cellulosic material and produce a characteristic oil when employed as a feed in the process of the invention. For example, municipal waste contains from 70 to 90% cellulosic material and produces a novel oil by the process of the present invention.

For purposes of this specification, the term "cellulosic material" means material containing cellulose or products derived from cellulose. Typical cellulosic materials include: paper, tree bark, sawdust, and vegetable waste, such as leached sugar cane, leached sugar beets, rice hulls, carrot tops, fruit skins, fruit pits, tree trimmings, leaves and like garden matter. Up to about 40%, and in some cases up to 85%, of the oil produced by the process from waste material containing not less than 70% by weight of cellulosic material is soluble in water. This oil is relatively insoluble in nonpolar solvents, such as carbon tetrachloride, heptane and decane. The oil contains from about 10 to about 15% titratable carboxylic acids, the acids having a pK_a of about 4.5. The viscosity of the oil is considerably higher than No. 6 fuel oil. The oil is soluble in acetone as well as other organic polar solvents such as methanol, ethanol and ethylene glycol. The oil has a relatively high pH of between about 1 and 3. The oil usually contains from about 10 to about 20% water which can be removed by distillation or extraction methods known to the art. The oil contains small amounts (less than 5%) of the following compounds: acetaldehyde, acrolein, furfural, 5 - methyl - 2 - furfuraldehyde, pyruvaldehyde, phenol, acetol, furfuryl, alcohol, methylethylketone, acetone, cyclohexanone, 2 - hydroxy - 3 - methyl - 2 - cyclopenten - 1 - one, acetic acid, formic acid, glycolic acid, lactic acid, dilactic acid, methyl formate, and 2 - methyl furan. The largest single chemical component of the oil is believed to be levoglucosan and other degradation products such as 5 - (hydroxymethyl) - furfuraldehyde, glucofuranose and glucopyranose, caused by the scission of the 1,4 glycoside linkages of cellulose followed by intramolecular rearrangement of the monomer units. Apparently, the heating of the hydroxyl groups of the cellulose matter during pyrolysis causes degradation of these groups to carboxyl groups rendering the resulting oil soluble in alkali and causing a series of colour changes of the resulting oil from yellow through reddish-brown and finally to black. All the oil produced to date from waste containing 70% or more cellulosic material has had a dark reddish-brown colour and is quite soluble in alkali. In fact, a dilute solution of caustic soda has been found to be an ideal solvent for removing the oil from surfaces, clothing and skin.

Elemental analysis of oils produced by the present process from waste materials contain-

ing organic matter, such as rubber tires, tree bark or cellulosic material, shows that the oil is made up of the following elements by weight: from about 40 to about 90% carbon, from about 2 to about 10% hydrogen, from 0 to about 40% oxygen, from 0 to about 4% sulphur, from about 0.1 to about 3% nitrogen, from 0 to about 1% chlorine. The oil has a heating value of from about 5000 to about 25,000 Btu/lb, a specific gravity of from about 1 to about 2. Up to 95% by weight of the oil is soluble in water.

Elemental analysis of the oil obtained from waste material containing about 70% cellulosic material shows that the oil is made up of the following elements by weight: from about 52% to about 60% carbon, from about

6% to about 8% hydrogen, from about 1% to about 2% nitrogen, from about 29% to about 33% oxygen and the remainder consisting of small amounts of sulphur, ash and chlorine. It is interesting to note that the elemental analysis of a typical municipal waste material shows that it contains about 46% carbon, about 6% hydrogen, about 6% ash, about 38% oxygen, and about 1% nitrogen with the remainder made up of smaller amounts of sulphur and chlorine. This indicates that during the pyrolysis of the process of the invention, a greater portion of oxygen is lost than any other element, probably as CO₂ and H₂O.

A typical analysis of the oil is presented in the following Table 3.

35

TABLE 3
Characteristics of Pyrolysis Products

Oil Characteristics		Nominal ⁺	Experimental Range [*]
Heating value:		4.8 × 10 ⁶ Btu/bbl	4.8 × 10 ⁶ —6.7 × 10 ⁶
Ash content:		0.2% (by wt.)	0.20—0.60
Ultimate analysis:			
Carbon		57.5% (by wt.)	54.5—70.6
Hydrogen		7.6	6.9 —9.3
Nitrogen		0.9	0.6 —1.5
Oxygen		33.4	18.9—33.4
Sulphur		0.1	0.10—0.20
Chlorine		0.3	0.08—0.41
Moisture content:		6.3% (by wt.)	4.2 —10.3
Flash point:		105°C ± 10° ⁺⁺	—
Density at 70°F:		1.3 gm/cc	—
Solubility tests:			
Percent by weight soluble in:			
Water:			84%
Pentane:			10%
Benzene:			47%
Quinoline:			100%
Char characteristics			
Heating value:		9,000 Btu/lb	6,000—9,700
Ash content:		31.8% (by wt.)	21.8—50
Ultimate Analysis:			
Carbon		48.8% (by wt.)	37.1—61.3
Hydrogen		3.9	2.0 —4.0
Nitrogen		1.1	1.0 —1.5
Oxygen		12.7	12.2—17.2
Sulphur		0.28	0.28—0.65
Chlorine		0.22	0.22—0.45
Moisture content:		0.6% (by wt.)	0.0 —1.44

⁺ Based on optimum conditions to date

^{*} Range depending upon process conditions

⁺⁺ Based on Cleveland Open Cup technique

As the above Table indicates, the oil produced by the process of the invention has a heating value comparable to that of No. 6 fuel oil (6.3×10^6 Btu/42 U.S. gal. bbl). The above Table also shows that the oil has a density appreciably greater than that of water. Thus spillage of the oil would not present the same ecological problems that most petroleum oils present. For example, if a tanker filled with the oil product of the process of the present invention ruptured a tank or accidentally discharged the oil into the sea, the oil would rapidly sink into the water and eventually dissolve in the water. Although tests have not been completed at the present time, it appears that the oil is biodegradable.

The following Examples serve to illustrate the invention. However, as will appear, not all the Examples describe operations that constitute embodiments of the process of the invention. For instance, Examples 1 to 4 and Examples 6 to 8 describe small-scale procedures capable of reproducing typical pyrolysis zone conditions of temperature rise rate, maximum temperature attained and residence period of the process of the invention without the use of hot char to supply heat to the waste solids in the pyrolysis zone as is required in full-scale operation. Likewise Examples 9 to 12 describe the results of applying the process conditions of the invention to certain pure chemicals that are common constituents of the waste solids that may be submitted to the process of the invention.

Example 1

A comminuted sample of municipal waste from Middleton, Ohio, U.S.A. was subjected to salvaging to remove nearly all the metal, glass and other inert materials, and about 50% of the paper fibers, and was then oven dried at 105°C. and pyrolyzed at 510°C. at atmospheric pressure. For this purpose, the dried, primarily organic, residue of this municipal solid waste was continuously fed into a small, bench-scale, pyrolysis reactor heated through its walls sufficiently intensely to heat the waste residue rapidly to the pyrolysis temperature. The waste residue was fed to the reactor at a rate of about three pounds per hour, and the particle size ranged from about 50 mesh (ASTM Standard-Tyler equivalent) to 1/2 inch. The average residence period was about 0.4 second at this feed rate. The results and chemical analyses are shown

in Table 4. The heating values are calculated from the chemical analyses.

TABLE 4

Char fraction,	heating value	
36.3 wt. %	9,700 Btu/lb	60
61.3 wt. %	Carbon	
2.8	Hydrogen	
1.5	Nitrogen	
0.4	Sulphur	
21.8	Ash	65
12.2	Oxygen (by difference)	
Oil fraction,	heating value	
28.8 wt. %	14,700 Btu/lb	
70.6 wt. %	Carbon	
9.3	Hydrogen	70
0.6	Nitrogen	
0.2	Sulphur	
0.4	Ash	
18.9	Oxygen (by difference)	
Gas fraction,	heating value	75
14.5 wt. %	260 Btu/cu ft.	
0.1 Mol %	Water	
22.2	Carbon monoxide	
63.2	Carbon dioxide	
2.1	Hydrogen	80
2.2	Methyl chloride	
6.2	Methane	
1.8	Ethane	
2.2	C ₁ to C ₈ hydrocarbon	

Water fraction 20.4 wt. %; contains methanol, acetic acid, etc. 85

Example 2

To illustrate the effect of pyrolysis on the same comminuted municipal solid wastes without prior paper fiber removal, but with the metal, glass and inert materials removed as in Example 1, the results shown below were determined:

Char fraction,	43.6 wt. %	
Oil fraction,	23.7 wt. %	95
Gas fraction,	13.5 wt. %	
Water fraction	19.2 wt. %	

Example 3

Municipal wastes having the composition shown in the following Table 5 were segregated into the three identified groups. 100

TABLE 5
Constituents in Municipal Solid Wastes

5	Component	Compiled by Solid Waste Management Office	Compiled by Black Clawson, Middletown, Ohio, U.S.A.
		Wt. % dry basis	Wt. %, dry basis
10	Group 1		
	Metals	11	
	Glass	10	
	Dirt	3	
	Sub total	24	27
15	Group 2		
	Food wastes	17	
	Plastics	5	
	Garden and like wastes	4	
	Cloth	3	
	Wood	2	
	Sub total	31	20
20	Group 3		
	Paper	45	53
	Total	100	100

The Groups 2 and 3 of the Black Clawson Company waste classification were combined and shredded to -24 mesh (Tyler) to yield a waste feed having about 90% of the inorganics removed. This waste feed was oven-dried to less than 5% moisture and pyrolyzed at about 500°C. at atmospheric pressure, without hydrogenation, in the manner described in Example 1 to yield products identified in Table 2 above.

Oils tested were the residue from a vacuum distillation removing acetone wherein the final solution temperature was approximately 52°C. Mass balance for the run producing the oil was 80%, and of the remaining 20% unrecovered mass, 1/5 is estimated to be due to distillation losses. It is estimated that 9 to 13% of the weight of the product oils was lost because of the low boiling fraction that boiled below 104°C.

Example 4

The oil fraction of Example 3 was subjected to atmospheric distillation to yield nine cuts which are identified in the following Table 6.

TABLE 6
Atmospheric Distillation of Solid Waste
Pyrolysis Oils

40	Cut	Distillation temperature range, °C	% by weight of product
	1	104 to 132	10.3
	2	132 to 160	9.9
	3	160 to 188	7.0
45	4	188 to 216	12.1
	5	216 to 243	3.5
	6	243 to 271	2.3
	7	271 to 299	1.3
	8	299 to 327	1.4
50	9	327 to 346	0.7
	Residue		32.4
	Loss + Holdup		19.1

Example 5

Segregated shredded municipal waste (+75% by weight cellulosic material, -10% inorganic matter) was subjected to pyrolysis in a manner similar to Example 1 but employing a turbulent gaseous stream comprising, by weight, 16 2/3% carrier gas, 16 2/3% particulate municipal waste (-10 mesh Tyler) and 16 1/3% particulate char, in the pyrolysis reactor. The particulate solid waste was heated to a temperature of about 510°C. and had a residence time of about 1.1 sec. in the pyrolysis reactor. The liquid organic chemical and fuel values, that is the oil product, had a moisture content of 20% by weight. The solubility of the oil was tested for several solvents and solutions, the results of which are shown in the following Table 7.

TABLE 7
Product Oil at 20% Moisture Content

	Solvent	% solubility of oil by weight
5	Aqueous caustic soda	99.5%
	Methanol	95
	Acetone	95
	Quinoline	98
	Water pH 4	63
10	pH 6	59
	pH 2	67
	Ammonia (pH 10)	70
	Benzene	8
	Toluene	8
15	Hexane	2
	Glycerol	15—40% depending on absence of large molecular weight organic chemical and fuel values

- Example 6
- 20 Shredded rubber tire material (69% carbon, 7% hydrogen, 0.3% nitrogen, 1.1% sulphur, 17.5% oxygen and 4.4% ash) was pyrolyzed in the manner described in Example 1 to obtain about 33% particulate char, about
- 25 17% gases (chemical and fuel values) and about 50% liquid (oil chemical and fuel values). Elemental analysis of the liquid (oil) values gave the following: carbon 83%, hydrogen 9%, nitrogen 0.7%, sulphur 1.1%,
- 30 oxygen 4.0% and ash less than 1%. The

specific gravity of the liquid was about 1, and the oil had a heating value of about 18,000 Btu/lb.

- Example 7
- 35 Tree bark from Douglas Fir was shredded to minus 24 mesh (Tyler) and pyrolyzed as described in Example 1. The products were 18% char, 48% oil, 20% gas, and 8% moisture. Elemental analysis of the products gave the following values:
- 40

	Char	Oil	Gas
45	Carbon	66.0%	60.7%
	Hydrogen	4.1%	8.0%
	Nitrogen	0.2%	0.2%
	Sulphur	.0%	.0%
	Ash	7.5%	0.05%
50	Chlorine	0.03%	0.01%
	Oxygen	22.0%	31.0%
	Carbon monoxide	—	47.1 vol. %
	Carbon dioxide	—	21.4 vol. %
	Methane	—	11.6%
	C ₂ H ₄ and C ₂ H ₆	—	5.8 vol. %
	C ₃ —C ₇ hydrocarbons	—	5.0%

The heating values of the products were as follows:

55	Char	11,500 Btu/lb
	Oil	12,000 Btu/lb
	Gas	500 Btu/cubic foot.

- Example 8
- 60 Rice hulls (37.7% carbon, 5.3% hydrogen, 0.4% nitrogen, 0.02% sulphur, 0.18% chlorine, 18.8% ash of which 78.9% was SiO₂, 33.5% oxygen and 4.1% H₂O) were shredded to —24 mesh (Tyler) and pyrolyzed at 500°C. in the manner described in
- 65 Example 1 to yield the following products: oil 31%, char 56% and gas 13%. The char was made up of 63.4% carbon, 2.0% hydrogen, 2.0% nitrogen, 0.5% sulphur,

0.11% chlorine, 27.4% ash (of which about 75% was SiO₂) and 4.6% oxygen.

70

- Example 9
- 75 Tetracosane (a common constituent of organic wastes) was ground to minus 100 mesh (Tyler) and pyrolyzed according to the present invention. The tetracosane was combined with a turbulent gaseous stream which was substantially free of oxygen and inert to the tetracosane. Hot, particulate char at

- 980°C. was added to the turbulent gaseous stream (5 pounds of char for each pound of tetracosane) and the entire mixture passed into a pyrolysis zone for a residence time of between 1 and 5 seconds to heat the tetracosane to a temperature of about 815°C. to form liquid chemical and fuel values. These values are rapidly cooled, after leaving the pyrolysis zone, to a temperature below 260°C.
- The elemental analysis of liquid chemical and fuel values so obtained was as follows: about 85% carbon, about 15% hydrogen and about 0% oxygen.

Example 10

- The method of Example 9 was repeated using 2 pounds of char to each pound of tetracosane and residence time of between 5 and 10 seconds to yield a liquid chemical and fuel value similar to that recovered in Example 9.

Example 11

- Naphthalene (another common organic waste constituent) was ground to powder (minus 80 mesh—Tyler) and combined with a carrier gas, substantially free of oxygen and inert to naphthalene, and hot char at 875°C. in the weight ratio 1:0.2:2 (naphthalene: carrier gas:char) to form a turbulent gaseous stream having a Reynolds flow Index Number of at least 2000. The stream was passed through a pyrolysis zone with a residence therein of about one second, during which the naphthalene attained about 500°C., and then passed to a cooling zone where the oil formed by the pyrolysis of the naphthalene was cooled to a temperature below 200°C. The oil had the following elemental analysis: about 94% carbon, about 6% hydrogen and about 0% oxygen.

Example 12

- The method of Example 11 was repeated employing a naphthalene:carrier gas:char ratio of 1:2:5 and a residence time of less than about 4 seconds, the naphthalene thereby attaining about 700°C., to obtain an oil very similar to the oil recovered in Example 11.

Example 13

- Sun dried cow manure (3% moisture) was shredded to minus one-quarter inch mesh and combined with a carrier gas containing about 1% by weight oxygen and hot char heated to a temperature of 620°C. to form a turbulent gaseous stream (Reynolds flow Index Number 3000). The weight ratio of particulate manure to gas to char is 1:1:4. The turbulent gaseous stream was passed through a pyrolysis zone with a residence time of about 0.8 seconds, the manure thereby attaining about 500°C., to form organic liquid values which were rapidly cooled, after leaving the pyrolysis zone, to a temperature below 235°C.

Example 14

Oven dried municipal waste (1% moisture) containing less than 5% metal, glass and other inorganic matter was shredded to minus one-eighth mesh and purged with nitrogen to remove oxygen therefrom. The waste, containing less than 1% oxygen, was fed into a pyrolysis reactor under a nitrogen atmosphere to prevent the admission of air and combined with a carrier gas, substantially free of oxygen and inert to the waste, and hot char ($T=735^{\circ}\text{C.}$) to form a turbulent gaseous stream (Reynolds flow Index Number of 2000+). The stream had a waste to gas to char ratio of 1:2:2. The turbulent gaseous stream was passed through a pyrolysis zone to heat the shredded waste to a temperature between 425°C. and about 510°C. to form organic chemical and fuel values. These values were rapidly cooled, after leaving the pyrolysis zone, to a temperature below 150°C. in a quench tower and recovered in a phase separation tank.

Example 15

The process of Example 13 was repeated employing a shredded manure:gas:char ratio of 1:1:10, the char being heated to a temperature of 1550°C. to heat the manure in the pyrolysis zone to a temperature of about 1400°C. The pyrolysis products were mainly gaseous.

WHAT WE CLAIM IS:—

1. A process for the production and recovery of chemical and fuel values from waste materials containing organic solids, comprising forming a turbulent stream (as herein defined) by entraining hot particulate char and particulate waste material, in an inert carrier gas (as herein defined); passing said stream through a pyrolysis zone at a rate such that the entrained solids remain in said zone for an average residence period not exceeding 10 seconds during which heat exchange takes place between the char and the waste material particles and the latter are heated to a pyrolysis temperature in the range 150 to 1400°C. to evolve volatile organic chemical and fuel values; and removing said chemical and fuel values from the stream leaving said pyrolysis zone.
2. A process according to Claim 1, including the step of rapidly cooling said removed organic chemical and fuel values to a temperature below the pyrolysis temperature so that further pyrolysis and degradation of said organic chemical and fuel values is minimized.
3. A process according to Claim 1 or 2, wherein the residence period of said waste material in the pyrolysis zone is less than one second.
4. A process according to any preceding claim, wherein said waste material is heated

- to a temperature in the range 315°C. to 565°C. in the pyrolysis zone.
5. A process according to claim 4, wherein said waste material is heated to a temperature in the range 425°C. to 510°C. in said pyrolysis zone.
6. A process according to any preceding claim, wherein said waste material is substantially free of inorganic matter.
7. A process according to any preceding claim, wherein the waste material has a maximum particulate dimension of less than one inch.
8. A process according to any preceding claim, including the steps of separating the particulate char from the stream leaving the pyrolysis zone; heating a portion of said separated particulate char to a temperature ranging from about 620°C. to about 980°C; and recycling said hot char to form said turbulent gas stream.
9. A process according to any preceding claim, wherein the said turbulent gas stream has a Reynolds Flow Index Number of at least 2500 in the pyrolysis zone.
10. A process according to any preceding claim, wherein said turbulent stream contains from 0.2 to 2 pounds of carrier gas for each pound of particulate waste material in said stream.
11. A process according to claim 10, wherein such an amount of particulate char is employed that said particulate waste material is heated to a temperature in the range 260 to 815°C. in said pyrolysis zone.
12. A process according to claim 11, wherein at least two pounds of hot particulate char is employed for each pound of particulate waste material in said turbulent gas stream.
13. A process according to any preceding claim, wherein the carrier gas is a hydrogen-enriched gas stream.
14. A process according to any preceding claim, wherein said waste material is a solid waste comprising municipal waste material, manure, sewage sludge, automobile tires, crude oil processing waste, agricultural waste, industrial waste, tree bark, rice hulls, or mixtures thereof.
15. A process according to any preceding claim, wherein said waste material has a moisture content of less than 5% by weight.
16. A process for the production and recovery of chemical and fuel values from waste materials, substantially as described with reference to the accompanying drawing.
17. Chemical and fuel values produced and recovered from waste material by the process of any preceding claim.

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1 SHEET

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